D.1 - Technologies for (in situ) remediation and management of soil contamination

STUDY OF THE IN SITU EFFICIENCY OF RANDOMLY-METHYLATED-B-CYCLODEXTRIN TO ACCELERATE SOIL FLUSHING TECHNOLOGY

Sniegowski[1] K., Vanhecke M.[2], D'Huys P-J.[2] and Braeken L.[1]

[1] Researchgroup Lab4U, Faculty of Industrial Engineering, Catholic University College Limburg associated with KU Leuven, Belgium
[2] Researchgroup Lab4U, Department of Industrial Science and Technology, Catholic University College Limburg associated with KU Leuven, Belgium

www.khlim.be/lab4U
kristel.sniegowski@khlim.be

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Introduction

Soil flushing with solubilizing agents is an interesting alternative for the frequently used pump & treat method for *in situ* soil remediation. Because of their low toxicity and biodegradability, the use of bio-based solubility enhancers, such as biosurfactants, is preferred over chemical additives such as cosolvent (Kosaric, 2001) and surfactants (Svab et al., 2009; Zhou and Zhu, 2008). A disadvantage of biosurfactants is however that their hydrophobic part adsorbs to the soil. This makes them less efficient in interacting with hydrophobic compounds and more difficult to recover from the soil for reuse. More suitable biobased solubilising agents for soil remediation are cyclodextrins (CD). CD are (α-1,4)-linked oligosaccharides with both an apolar cavity and polar exterior and are able to encapsulate hydrophobic contaminants (Figure 1) thereby enhancing their solubility and accelerating the soil flushing process (Berselli et al., 2006). In addition, by enhancing the water solubility, apolair contaminants become more bioavailable, accelerating the bioremediation process (Gan et al., 2009; McCray et al., 2000). Because of their cyclic structure, CD, in contrast to biosurfactants, adsorb very little to the soil surface (Brusseau et al., 1994; Zeng et al., 2006), which makes it more easy to reuse cyclodextrin solutions after usage. In addition, they don't increase the hydrofobicity of the soil surface thereby decreasing the solubilisation of the contaminants (Fenyvesi et al., 2009).

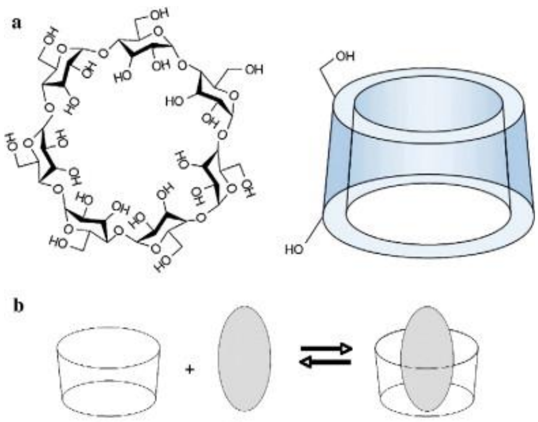

Figure 1: Schematic view of (a) the structure of cyclodextrin and (b) mechanism of inclusion formation with a molecule (Devis and Brewster, 2004).

A lot of research has been published regarding the enhancement of the water solubility and/or bioavailability of contaminants with CD for a wide range of contaminants such as PCB (Balogh et al., 2007), trichloroethylene (Fenyvesi et al. 2010), polycyclic aromatic hydrocarbons (Viglianti et al., 2006;

Wang et al., 2005) and pesticides (Morillo et al. 2001, Wong and Bidleman 2010). In addition, some field trials to test soil flushing with CD obtained good results (Boving et al., 1998, McCray and Brusseau, 1998).

Despite their high potential, CD are relative expensive to use for soil remediation purposes because high quality CD are nowadays mainly produced for applications in the pharmaceutical industry, food industry, cosmetics, agricultural industry and chemical industry (Del Valle, 2004). In order to make the use of CD economically more interesting for soil remediation, it is necessary to investigate the conditions which affect the efficiency of CD in order to correctly estimate the costs of using CD in soil remediation. Previous research looked into the K_{ow} and K_{oCD} distribution coefficient in order to compare the efficiency of different cyclodextrins (Fenyvesi et al., 2009). Although this is an easy method, it is less relevant to estimate the mobilization of contaminants by CD under *in situ* conditions. CD can indeed complexate other organic compounds from the soil, such as humic acids (Praus et al., 2004; Abner et al., 2004). In relation to this, Ishiwata and Kamiya (1999a, b) observed less complexation of organophosphorus pesticides in the presence of humic acids due to competition for CD (Ishiwata and Kamiya 1999a, b). However, only a small amount of publications regarding this topic are available.

The aim of this research is to evaluate the efficiency of CD at different soil/water ratio's to investigate the effect of soil on the uptake capacity of CD. Therefore, three different 'solubility' experiments, with respectively water, soil/water (1/10) and soil/water (3/1) were performed. Because studies regarding the remediation of soils contaminated with mineral oil (MO) using CD are rare and many soils in Flanders (Belgium) are contaminated with MO, a soil contaminated with diesel was used to investigate the capacity of CD to capture MO. Furthermore, randomly-methylated-β-cyclodextrin was selected as CD since it has a high potential to be used in the remediation of soil because of its non-toxicity, long half-time (1-2 years) and high removal efficiency (own data, not published).

Materials and Methods

Randomly-methylated-β-cyclodextrin (CD) was obtained from Wacker Chemie (Germany, technical grade). The soil used for the soil/water experiments was contaminated with diesel and contained 2492 mg MO/kg (dry weight), 3.9 % organic matter, 95.3 % sand and 85.5 % dry matter. The soil was sieved over 4 mm before usage.

In the first experiment the solubility of MO (diesel) in tap water containing different concentrations of CD was determined. Diesel (10.5 g) was added to 1000 mL of water to achieve oversaturation and a layer of diesel became visible. After shaking for 1h, 900 mL of water was separated from the solution and the amount of dissolved MO was measured with GC-FID after liquid-liquid extraction with hexane. The extract was concentrated by evaporating the hexane until 1 mL. A mixture of C10 and C40 was added to the extract to define the boundaries of the mineral oil peaks in the chromatogram. Mineral oil was separated using a GC-FID (Agilent) and a DB-5ms column (30 m x 0.25 mm, 0.25 µm). Volumes of 1 µL were injected on the column with helium as carrier gas. The initial temperature of 50 °C increased after 3 min with 25 °C/min until 315 °C was obtained. After 20 min, the temperature decreased again until 50 °C. The area sum between C10 and C40 was used to determine the concentration of mineral oil in the sample. The concentration of mineral oil was calculated based on a calibration curve made with a standard mineral oil solution from the Dutch institute of public health and the environment (RIVM).

In the second experiment 50 g of soil contaminated with 2492 mg/kg MO (diesel) was mixed with 500 mL of either clean tap water or tap water containing 50 g/L CD. As such, a soil/water ratio of 1/10 was obtained. After shaking for 24h, the soil was removed by filtering and the amount of MO was analyzed in the aqueous soil extract as previously described. In an additional assay the experiment was repeated to measure the amount of dissolved organic carbon (DOC) in the soil extract. Therefore, after 24 h of shaking, a sample of 2 mL was filtered over 0.45 µm and the absorbance at 254 nm was measured. The amount of absorbance is correlated with the concentration of DOC in the water sample. As a control, a sample of CD (50 g/L) was measured the same way.

In the final experiment, 500 g (wet weight) of the same soil was packed in a glass column (5 cm i.d. x 20 cm) and from the bottom filled with 1.5 pore volumes of tap water. The density of the soil in the column was 1.23 g/cm³. After 24 h of conditioning, the water was replaced with either the 0 or 50 g/L CD solution for 1 week using a peristaltic pump set at a flow rate of 10 mL/h. This corresponds to a pore water velocity of 2.5 cm/h. The flow rate was maintained for 8.5 h, followed by period of 3.5 h with the pump turned off. By repeating this cycle, the columns were flushed 16 times with either tap water or a CD solution during one week. Taking into account the amount of water in the soil, the soil/water ratio was approximately 3/1. After one week, the cumulated concentration of MO in the collected effluent water was determined.
The three experiments were performed in triplicate. The uptake capacity of CD was calculated as the amount of MO in solution (mg) per g of CD.

Results

Efficiency of CD to dissolve MO in water

Adding CD to the solution definitely enhances the water solubility of MO (Figure 2). Without CD the average water solubility of diesel is 2 mg/L. With 10 g/L of CD the concentration of dissolved MO is 1.5 times higher than without CD. Concentrations lower than 10 g/L did not enhance the water solubility of MO, but on the contrary, it seemed that the concentration of MO stayed below the reference water solubility. At concentrations higher than 10 g/L, the concentration of dissolved MO increases linearly concomitant with the concentration of CD. At 50 g/L CD the amount of MO dissolved in water was 5.0 times higher than in absence of CD.

The calculated average uptake capacity depended on the concentration of CD used. The higher the concentration of CD, the lower the ‘apparent’ uptake capacity of CD. This is caused by the water solubility of MO in water without CD. At low concentrations of CD, the water mainly contains dissociated MO (MO that has not formed an inclusion complex with CD). At higher CD concentrations (> 10 g/L), when the amount of dissolved MO is significantly higher compared to the water solubility of MO in absence of CD, MO molecules are merely present as a complex with CD. As such, the uptake capacity decreases to a stable value of 0.2 mg/g. It is therefore suggested that the uptake capacity of CD can only be correctly estimated using high concentrations of CD or that the amount of dissociated MO is taken into account when calculating the uptake capacity at low concentrations of CD.

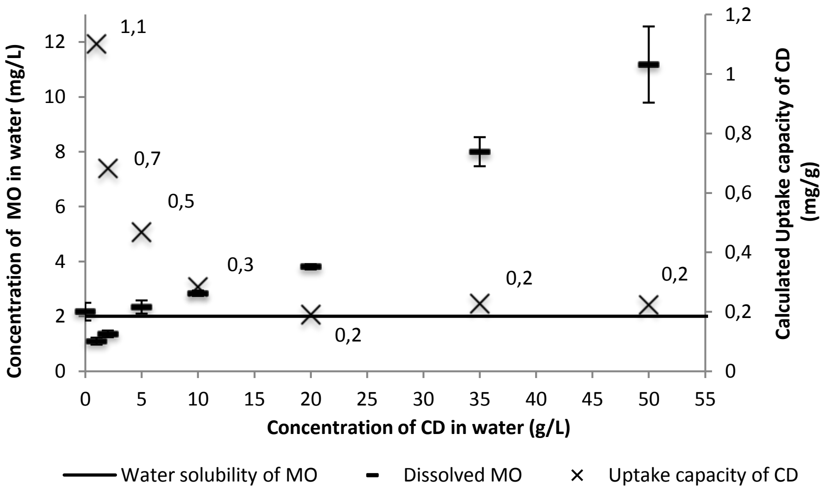

Figure 2: Amount of mineral oil (diesel) dissolved in water (-) and the calculated uptake capacity of cyclodextrin (x) at different concentrations of cyclodextrin.

Efficiency of CD to dissolve MO in soil water.

Whether or not the efficiency of cyclodextrin is affected by the presence of soil in the water was investigated in the following tests, using different soil/water ratio's. Figure 3 gives an overview of the results regarding the dissolution of MO in water and the uptake capacity of CD. The amount of MO dissolved in the aqueous soil extract containing 50 g/L CD was significantly higher (45 – 55 mg/L) than in a CD solution without soil (9.6 – 12.8 mg/L). This means that 0.9 mg of MO could be taken up per gram of CD instead of 0.2 mg/g in clean water. In addition, the amount of MO found in the soil extract without CD was 50 times less (0.46 – 1.0 mg/L). In the column flushing experiment (average soil/water ratio of 3/1), the average concentration of MO in soil water varied between 163,7 - 197,9 mg/L. In contrast, the columns flushed with clean tap water only dissolved 0.51 – 0.87 mg/L MO. This means that the uptake capacity of CD reached 3.6 mg/g.

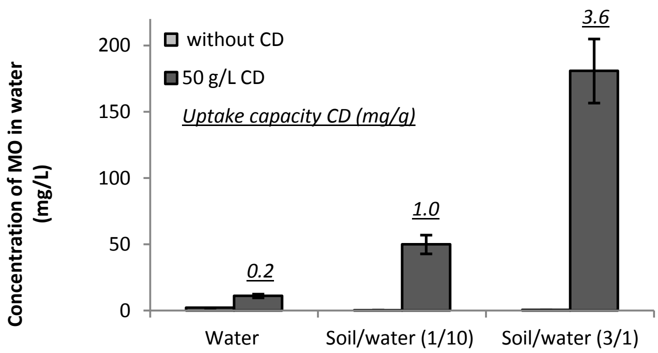

Figure 3: Amount of dissolved MO and calculated average uptake capacity of CD (50 g/L) at different soil/water ratio's.

The results clearly show that the presence of soil positively affects the uptake capacity of CD for MO. We hypothesize that this increased efficiency is due to the fact that CD dissolves indeed not only mineral oil but also organic matter, thereby increasing the dissolved organic carbon (DOC) content in the aqueous soil extract. Additional measurements confirmed that the absorbance at 254 nm of filtered soil water, which is an indication of the amount of DOC, increased 3 times due to the presence of CD (50 g/L) in the solution. The composition of DOC is very complex with both hydrophilic and hydrophobic structures, which can also complexate with MO. The observed synergetic effect might indicate that the mobilized DOC by complexation with CD, in turn, enhances the amount of dissolved MO. Several publications indeed show that DOC can mobilize hydrophobic compounds such as PAHs (McKay and Gschwend 2001), pesticides (Chiou et al. 1986) and petroleum hydrocarbons (Chen et al. 2008). However, this seems to be in contrast with previous results (Ishiwata and Kamiya, 1999 a, b) where a negative effect was observed because of the competition for CD. Since the DOC was not further characterized in this study, the exact mechanism remains unclear and further investigation is required.

Conclusion

This study was able to investigate the efficiency of CD to dissolve MO in the water and the uptake capacity of CD for MO in order to use it as solubility enhancer for *in situ* soil remediation. The capacity of CD ranged between 0.2 and 3.6 mg/g and depended on the soil/water ratio. Increasing the soil/water ratio increased the calculated uptake capacity of CD. We hypothesize that CD also increased the amount of dissolved organic matter in the aqueous soil extract, thereby further enhancing the solubility of MO. However, more investigation is needed to look into the mechanism of this phenomenon. For example, further experiments might look into the effect of the type of soil (and the type of dissolved organic matter) on the uptake capacity of CD. In addition, it would be interesting to compare the uptake capacity of different types of cyclodextrin in order to determine their *in situ* potential for soil flushing.

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